Crystallization kinetics of polypropylenes. Effect of nucleating agents?

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ABSTRACT:
Thermal conditions and formulation affect the crystallization mechanisms of polymers and the associated kinetics in a coupled manner. In that field, the objective of this investigation is to compare overall crystallization kinetics and structural organization of one clarified polypropylene (specifically designed for stretch-blow molding) and a homopolypropylene. Liquid/solid transitions are investigated *in-* and *ex-situ* under isothermal and non-isothermal conditions combining crossed-polarized optical microscopy, differential scanning calorimetry and X-ray diffraction. Clarified polypropylene has a very 'singular behavior' compared to homopolymer since no spherulites can be observed. However, it exhibits a semi-crystalline structure. The major α-phase coexists with some γ-phase even under quiescent conditions. Overall crystallization kinetics is rapid suggesting the existence of very efficient nucleating agent(s) and resulting in an increase of crystallization temperature. In parallel, the melting temperature of copolymer decreases by 20 °C compared to homopolymer, suggesting a drastic change in lamellae thickness. It is concluded that this unusual structure results from nucleation, which enforces high temperature crystallization, and copolymerization, which constraints the crystalline organization.

Key words: Crystallization, Polypropylenes, Nucleating agents, Modeling.

INTRODUCTION

The processing of polymers always requires newly formulated polymers with some special characteristics. Especially, polypropylene is one of the semicrystalline polymers that exhibits pronounced polymorphs and morphologies depending on its tacticity, thermal treatments, and mechanical handling. Nucleating agents are used in order to improve stiffness, transparency and cycle time. They raise the crystallization temperature and shorten the injection molding cycle time. They initiate a higher number of crystallization sites thus reducing the spherulite size. They cause simultaneous growth and evenly sized crystals [1,2,3].
The description of liquid/solid transitions is required to understand structure development of polymers during crystallization. The macroscopic theory of crystallization kinetics as formulated by Avrami and applied to polymers is the most popular to analyze the changes in nucleation and growth processes. The transformed volume fraction α(t) as a function of time t is given by the equation (1)

$$\alpha(t) = 1 - \exp\left(-k_a t^{n_a}\right) \qquad (1)$$

where k_a and n_a are Avrami's crystallization rate constant and exponent respectively. To take into account the temperature change in Avrami's model, numerical methods were developed [4,5].

Consequently, evaluation of development of crystallinity as a function of temperature will be presented using a combination of various experimental techniques, such as *in-situ* polarizing optical microscopy, differential scanning calorimetry, wide angle X-ray diffraction.

1 EXPERIMENTAL

1.1 Materials

Two kinds of polypropylene were investigated. An isotactic homopolymer polypropylene (melting point 165 °C, Melt Flow Index MFI 25) was supplied by ATOFINA Company (France) under the reference PPH 3250 MR1. It is suitable for injection molding. A clarified copolymer polypropylene under the

reference PPR 7225 (melting point 146 °C, MFI 10) was obtained from Total Petrochemicals (Belgium). It is designed for injection stretch-blow molding.

1.2 Techniques and Methods

1.2.a Polarizing Optical Microscopy (POM)

The crystallization events and morphological features were observed *in-situ* by crossed-polarized optical microscopy with a polarizing LEICA-DMRX microscope (Leica-microsystemes, France) coupled with a hot-stage. The transparent hot-stage type Mettler FP82 was used to generate a controlled thermal history. A constant nitrogen flux compensates for heat losses and reduces polymer oxidation. Calibration of the hot stage was performed by measuring the melting point of benzoic acid. Thin layers of polymers (thickness of 100 μm) were investigated. For each study a new sample was used. The molten polymer was maintained at 210 °C during 5 min and cooled at -10 °C.min^{-1} down to the crystallization temperatures of (126, 130, 136, 140) and (126, 130, 136, 140, 146, 150) °C respectively for the homo and copolymer isothermal studies, or at modest cooling-rates (12, 10, 7, 5, 2, 1) °C.min^{-1} down to the end of crystallization, for non-isothermal studies. The measurement of the depolarized light intensity allows us to monitor the overall kinetics under both controlled thermal and non-isothermal conditions. The overall kinetics of crystallization $\alpha(t)$ is defined by the equation (2)

$$\alpha(t) = \frac{I(t) - I(0)}{I_\infty - I(0)} \qquad (2)$$

where I(t) is the transmitted intensity, I(0) the intensity prior to crystallization and I_∞ the maximum intensity observed at the end of crystallization.

1.2.b Differential Scanning Calorimetry DSC

Differential scanning calorimetry measurements have been carried out using a PERKIN-ELMER DSC 7 calorimeter. The weight of the sample was about 11 mg with a thickness of about 600 μm. The experiments were carried out under nitrogen. The instrument was calibrated with indium standard for temperature and heat change. The sample were melted at a heating rate of 10°C.min^{-1} to 210°C and maintained at this temperature for 5 min in order to erase the thermal history of the polymer. Then, the polymer was cooled from 210 to 50 °C at modest cooling-rates ranging from 0.1 to 20 °C.min^{-1} same as POM investigations. This procedure was repeated two times and only the second heating and cooling were used for calculation. The temperature reading shown by DSC is that of the polymer sample itself, so that the process is investigated with greater confidence.

When applied for DSC use, it is assumed that the differential area under the crystallization curve with time corresponds to the dynamic changes in the conversion of mass from the melt phase to the solid phase. Based on the heat effects, the relative crystal conversion $\alpha(t)$ as a function of time was calculated by the equation (3).

$$\alpha(t) = \frac{Q(t)}{Q_\infty} \qquad (3)$$

where Q(t) is the heat liberated until time t and Q_∞ is the total heat liberated by crystallization.

1.2.c WAXS measurement

The structure of PP was analyzed by means of wide angle X-ray scattering (WAXS). The X-ray diffraction measurements were performed with a CuK_α radiation (wavelength λ = 0.1542 nm) from a Philips X'pert X-ray diffractometer (40 kV, 30 mA). The intensity was measured as a function of the scattering angle 2θ in the range of 10 to 50°. The films prepared for optical measurements were analyzed.

2 RESULTS AND DISCUSSION

2.1 Isothermal Overall kinetics

The general features of polymer crystallization were followed with POM technique. The *in-situ* observation of the crystallization shows that clarified polypropylene has a very 'singular behavior' compared to homopolymer since no spherulite appears (Figure 1). For copolymer, crystallization occurs essentially in the 'first post-nucleation stage': bundle-like nuclei appear with time. Numerous crystallization sites appear and no crystal growth is observed. The observation has to be confirmed with microtomed cross-sections of DSC specimen. From the optical observations unlike homopolymer, with such a copolymer it is not possible to quantify directly the key kinetic parameters, namely $N_0(T(t))$

the initial density of potential nuclei, their activation frequency q(T(t)) and G(T(t)) the growth rate of the semi-crystalline entities, needed for modeling crystallization process [5].

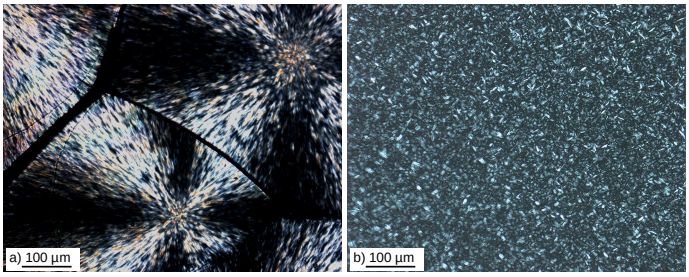

Fig. 1. Morphology development of : a) homopolymer PP3520 at 136 °C (110 µm-thick layer), b) copolymer PP7225 at 146 °C (12 µm-thick layer).

Nevertheless, overall kinetics can be defined (Equation (2)). From the curves of $\alpha(t) = f(t)$, half-time of crystallization ($t_{0.5}$) was determined as the time when crystal conversion was 50% (Figure 2). The half-time $t_{0.5}$ increased with increasing crystallization temperature. Copolymer shows a higher crystallization temperature and crystallizes faster than homopolymer that suggesting the existence of very efficient nucleating agent(s).

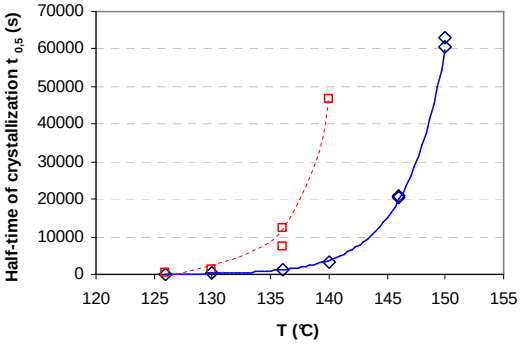

Fig. 2. Half-time of crystallization as a function of isothermal conditions: □, PP3250; ◊, PP7225.

Avrami's coefficient n_a calculated from $\ln[-\ln(1-\alpha(t))]$ against $\ln(t)$, in the selected range $0.2 < \alpha(t) < 0.4$, gives $n = 2.9$, which corresponds to a 3D condition.

2.2 Non-isothermal Overall kinetics

Non-isothermal crystallization was followed with both POM and DSC techniques. The relative crystal conversion $\alpha(t)$ obtained by DSC is plotted as a function of temperature for modest cooling-rates (Figure 3). The sigmoid shape of the overall kinetics is typical of the nucleation and growth crystallization process. If we neglect the thermal gradient (same sample thickness) one can see that the higher the cooling rate is, the higher the decrease in the temperature crystallization is. The relative crystal conversion of the copolymer occurs at higher temperature by 8 °C compared to homopolymer.

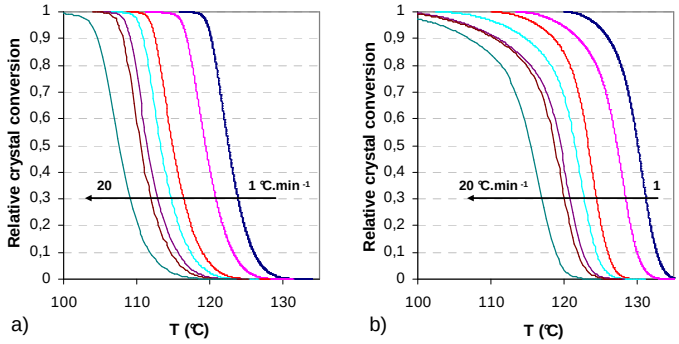

Fig. 3. Non-isothermal crystallization conversion investigated by DSC on: a) homopolymer, b) copolymer.

At the end of crystallization, when $\alpha(t)$ tends to 1, the conversion of copolymer becomes slower. The same pattern was observed with POM experiments. Then, it becomes difficult to exactly determine the end of crystallization. In the case of homopolymer, the end of crystallization is more precisely defined: with optical observation spherulites merge with their first neighbors, with DSC the baseline is reached more quickly (Figure 4-down).

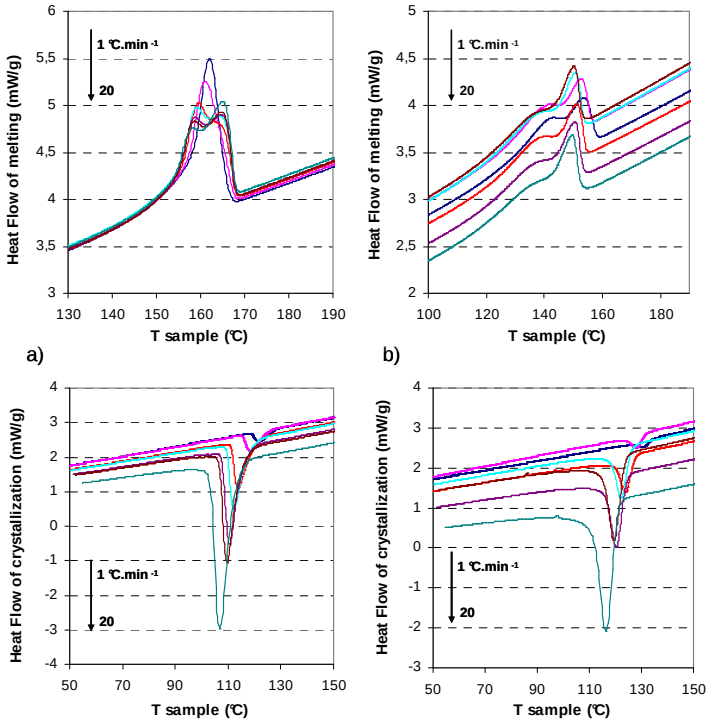

Fig. 4. Melting and crystallization heat flow: a) homo-, b) co-polymer, after a first cooling at (1, 2, 5, 7, 10, 12, 20) °C.min^{-1}.

Figure 4 illustrates the evolution of the heat flow as a function of the polymer temperature during the heating before the crystallization and the subsequent

crystallization. It was observed that homopolymer shows two peaks (melting). The main peak at 165 °C is caused by melting of monoclinic α-phase whereas the hexagonal β-phase melt at about 159 °C. We also suppose to have two families of lamellae that also give a double peak [6]. Copolymer seems to have two polymorphs identified by WAXS analysis.

2.3 Polymorphism patterns

WAXS analysis was performed to study the effect of cooling rates with the polymorph patterns of the polymers (Figure 5). Positions of the diffraction peaks indicate different crystal modifications. Polypropylenes have three different crystalline structures designated as α-form, β-form and γ-form. In agreement with DSC data, β-peak is identified for homopolymer at 2θ = 16° [7]. WAXS pattern of copolymer shows a peak at 2θ = 20°. This peak most probably indicates the presence of γ-form.

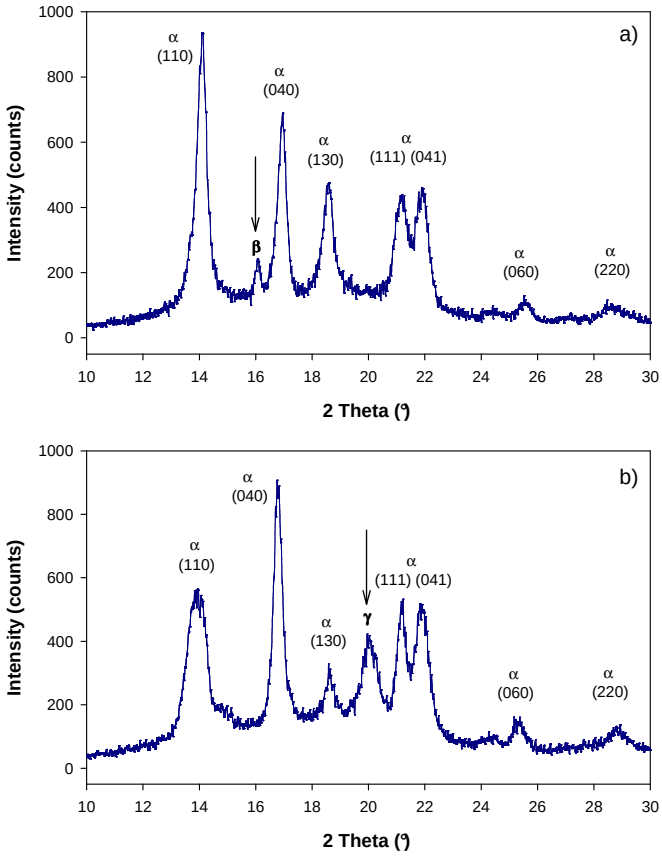

Fig. 5. WAXS patterns of: a) homopolymer, b) copolymer; after cooling-rate at 12 °C.min^{-1}.

It is supposed a competitive effect between nucleation and copolymerization. Nucleating agent(s) favor the high temperature nucleation whereas copolymerization constraints the crystalline organization during crystallization.

3 CONCLUSIONS

A first approach to study the effect of nucleating agent(s) on crystallization is studied using POM, DSC and WAXS. Compared to homopolymer, clarified copolymer does not crystallized with a spherulite-form and shows a mixed α- and γ-form crystalline structure.

As well as the nature of nucleating agents is not known, it remains difficult to distinguish the exact role of active γ-phase nucleating agent(s) or copolymer organization.

Further investigations need to analyze in details the effect of nucleating agent(s), especially the lamellae thickness with electron microscopy.

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